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Nonlinear dynamics of melted polymer layers

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Abstract

A theory for non-linear rheology of molten polymer layers between solid surfaces in the Rouse regime is discussed. It is shown that the effect of finite extensibility of polymer chains leads to the characteristic $1/3$ power law for the shear stress vs. shear velocity in the regime of high velocities. It is also shown that bridging polymer fragments connecting the two surfaces play an important role for the rheology if the effective monomer friction in the immediate vicinity of the surfaces is much higher than far from the surfaces. In particular we predict that shear stress is decreasing with shear velocity u in a limited range between u_1 and u_{\min} . This effect results in a possibility of stick-slip periodical dynamics of the layer under a constant imposed velocity.

1. Introduction

Polymer liquids show very rich and complex rheological behavior [1-3]. While recent research efforts were focused on dynamics of high-molecular-weight (entangled) polymers in the bulk [3,2], it was also recognized that rheology of confined polymer systems differs significantly from the bulk polymers even if the chains are short and not entangled ($M < M_e$). In particular, experiments show that confined polymer nano-layers show non-linear rheological behavior at much smaller shear rates than their bulk counterparts [4-8]. One of the important factors that controls rheology of polymer films is the surface - monomer interaction. In the case of attractive interaction polymer forms thin virtually adsorbed "glassy" layers near each surface. The effective monomer friction in these "glassy" layer is normally much higher than in the bulk.

The aim of the present article is to review some recent theoretical approaches [9-12] to non-linear rheology of confined unentangled polymer melts. The stress vs. shear rate dependencies will be considered first for the bulk systems (next section) or for thick films (film thickness h is larger than polymer size R), where a new theory of Rouse polymer dynamics taking into account non-Gaussian chain elasticity is described. The case of thin films ($h \ll R$) is considered for the regimes of moderate and high surface frictions in sections 3 and 4 respectively. In particular the role of bridging polymer fragments is analyzed in detail. A theory of stick-slip sliding motion in thin polymer films is presented in the last section. In all the cases the theoretical treatment is limited by a scaling accuracy, and the numerical prefactors in scaling dependencies are entirely ignored.

2. Nonlinear rheology in the bulk

Rouse model

Let us consider a melt of polymer chains in the regime of no entanglements: number of links per chain N smaller than N_e (=number of links per entanglement), $N < N_e$. Polymer contribution to stress tensor can be generally represented as [1,3]: $\sigma_{\alpha\beta} = c \sum_{n=1}^N \langle f_{\alpha}^{(n)} r_{\beta}^{(n)} \rangle$, where $c = \frac{1}{Nv}$ is concentration of polymer chains (Nv is the effective volume per chain), $\alpha, \beta = 1, 2, 3$ enumerate the Cartesian coordinates, $\mathbf{r}^{(n)}$ is the position of the n -th monomer of a chain, and $\mathbf{f}^{(n)}$ is the dissipative (friction) force acting on the n -th monomer, and $\langle \rangle$ means averaging over all chains.¹

Let us impose a hydrodynamic shear flow field, $\mathbf{u}_x = \dot{\gamma}z$, $\mathbf{u}_y = \mathbf{u}_z = 0$. The friction force acting on a monomer is $\mathbf{f} = \zeta_0 \Delta \mathbf{u}$, where $\Delta \mathbf{u}$ is the difference between the flow velocity and the monomer velocity.

It is convenient to define the coordinate system so that its origin coincides with the centre of mass of a polymer chain. The velocity of all monomers of this chain is then zero on the average since the flow is stationary, so that $f_x = \zeta_0 \Delta u_x \simeq \zeta_0 u_x = \zeta_0 \dot{\gamma}z$, and shear stress is

¹Note that the total force acting on a monomer is a sum of $\mathbf{f} + \mathbf{f}'$, where \mathbf{f}' is the total conservative force (due to the polymer chain elasticity). Since inertial effects are normally absolutely negligible for polymer dynamics, the total force is zero, so that $\mathbf{f}' = -\mathbf{f}$.

$$\sigma_{zz} = c\dot{\gamma}\zeta_0 \left\langle \sum_{n=1}^N z(n)z(n) \right\rangle \sim c\dot{\gamma}\zeta_0 N R_z^2 \quad (1)$$

where R_z is the chain size in z-direction. Taking into account that $R_z^2 \sim R^2$, where $R = N^{1/2}a$ is the equilibrium size (end-to-end distance) of a polymer coil in the melt (a is the polymer statistical segment), we estimate the shear stress as

$$\sigma_{zz} \sim \zeta_0 c \dot{\gamma} N^2 a^2 = \frac{1}{v} \zeta_0 N a^2 \dot{\gamma} \quad (2)$$

The hydrodynamic friction force is acting in x-direction. Therefore the force does not perturb the coil size in z-direction, since polymer chains in the melt state are characterized by Gaussian elasticity. Thus eq. (2) formally holds for any shear rate $\dot{\gamma}$, implying that shear viscosity is independent of shear rate

$$\eta_0 \sim \frac{1}{v} \zeta_0 N a^2 \quad (3)$$

which is a well-known result of the standard Rouse theory [3].

The total friction force acting on, say, half of a chain in the flow (x) direction is

$$F_x \sim N f_x \sim N \zeta_0 \dot{\gamma} R_z$$

where R_z is the chain size in z-direction. This force stretches the chain in x-direction by

$$\Delta R_x \sim F_x N a^2 \sim N^2 a^2 \zeta_0 \dot{\gamma} R_z \quad (4)$$

(here and below we consider the thermal energy $k_B T$ as energy unit). Employing a dumb-bell picture of a polymer chain (two halves of the chain are substituted by material points separated by $\Delta \mathbf{R}$) we get the xx-stress component, $\sigma_{xx} \sim c \langle F_x \Delta R_x \rangle \sim \frac{1}{v} N^3 (\dot{\gamma} \tau_0)^2$, where $\tau_0 = \zeta_0 a^2$ is the monomer time. Thus we get the well-known [3] result for the first normal stress

$$N_1 = \sigma_{xx} - \sigma_{zz} \simeq \sigma_{xx} \sim \frac{1}{v} N^3 (\dot{\gamma} \tau_0)^2$$

Finite extensibility of chains

Let us now take into account that as the flow stretches the chain more and more, its elasticity should start to deviate from of an ideal Gaussian coil. In particular the chain can not be stretched more than its total contour length $L \sim Na$. Therefore eq. (4) is valid only if $\Delta R_x \ll L$, or if $\dot{\gamma} \ll \dot{\gamma}^* = \frac{1}{\tau_0} N^{-3/2}$. In the opposite regime $\dot{\gamma} \gg \dot{\gamma}^*$, the flow field could nearly completely stretch the chain in the x-direction, so that $R_x \simeq Na$. Simultaneously the chain is compressed in two other directions. In order to estimate, say, R_z , we note that the typical chain tension P must be of order $F_x \sim N \zeta_0 \dot{\gamma} R_z$. Therefore the total force acting on half of the chain in z-direction is $P_z = -P \tan \alpha \sim F_x R_z / R_x$, where α is the angle between the stretched chain and x-axis, $\tan \alpha = R_z / R_x$. Thus we get $P_z = -A R_z$, where $A = F_x / (Na)$. The corresponding effective potential is $U^*(R_z) = \frac{1}{2} A R_z^2$. The typical value of R_z due to thermal fluctuations is determined by the condition $U^*(R_z) \sim 1$ (in $k_B T$ units), which can be rewritten as

$$R_z^2 \sim \frac{a}{\zeta_0 R_x \dot{\gamma}} \quad (5)$$

so that $R_z \sim a(\dot{\gamma}\tau_0)^{-1/3} = R(\dot{\gamma}/\dot{\gamma}^*)^{-1/3}$. Eq. (5) is valid if the effect of flow on R_z is strong, i.e. for the regime $\dot{\gamma} \gg \dot{\gamma}^*$, where $R_z \ll R = N^{1/2}a$. In this regime the *global* chain conformation is essentially non-Gaussian in all directions. However small parts of the chain still obey Gaussian statistics in z-direction. In particular the transverse dimension of a segment consisting ΔN monomers is $R_z(\Delta N) \sim a(\Delta N)^{1/2}$ if $\Delta N < g$, where g is the number of links per characteristic hydrodynamic "stretched blob" which is defined by the condition $\dot{\gamma}^*(g) = \frac{1}{\tau_0}g^{-3/2} = \dot{\gamma}$, so that $g \sim (\dot{\gamma}\tau_0)^{-2/3}$. Note that the shape of a "stretched blob" is strongly asymmetric: $R_x(g) \sim ag \sim a(\dot{\gamma}\tau_0)^{-2/3}$, $R_z(g) \sim R_y(g) \sim a(\dot{\gamma}\tau_0)^{-1/3}$, $R_x(g) \gg R_z(g)$. The typical hydrodynamic force acting on a stretched blob is $F_z(g) \sim 1/a$, so that the blobs are really nearly completely stretched along the flow. The chain conformation on scales larger than g can be represented as a linear sequence of "stretched blobs": the size along the flow, R_x , is proportional to the number of blobs, N/g , and the transverse size is nearly *independent* on the number of blobs: $R_z(g) \sim R_z(N)$. Of course conformation of a chain and its sizes are strongly fluctuating with some characteristic frequency [9]. In particular the chain is not completely stretched along the flow all the time, but rather roughly half of the time; another half of the time the chain is moderately stretched.

Thus the scaling dependence of the transverse size on the shear rate is

$$R_z \sim \begin{cases} N^{1/2}a & , \dot{\gamma} < \dot{\gamma}^* \\ a/(\dot{\gamma}\tau_0)^{2/3} & , \dot{\gamma} > \dot{\gamma}^* \end{cases} \quad (6)$$

Using eqs. (1), (6) we get the shear stress

$$\sigma_{xz} = \begin{cases} \eta_0 \dot{\gamma} & , \dot{\gamma} < \dot{\gamma}^* \\ \frac{1}{v} (\dot{\gamma}\tau_0)^{1/3} & , \dot{\gamma} > \dot{\gamma}^* \end{cases} \quad (7)$$

and nonlinear shear viscosity

$$\eta \equiv \frac{\sigma_{xz}}{\dot{\gamma}} \sim \begin{cases} \eta_0 & , \dot{\gamma} < \dot{\gamma}^* \\ \eta_0 (\dot{\gamma}/\dot{\gamma}^*)^{-2/3} & , \dot{\gamma} > \dot{\gamma}^* \end{cases} \quad (8)$$

where η_0 is defined in eq. (3). Thus we predict shear thinning with $-2/3$ power law [9]. Note that although this viscosity behavior is often observed experimentally [1], most of the data concern systems in entangled regime rather than Rouse regime.

The effect of a finite chain extensibility is also revealed in the shear rate dependencies of normal stress differences. With the same arguments as above we get:

$$N_1 \sim \begin{cases} \frac{1}{v} N^3 (\dot{\gamma}\tau_0)^2 & , \dot{\gamma} < \dot{\gamma}^* \\ \frac{N}{v} (\dot{\gamma}\tau_0)^{2/3} & , \dot{\gamma} > \dot{\gamma}^* \end{cases}$$

The second normal stress difference, $N_2 \equiv \sigma_{xx} - \sigma_{yy}$, is known to be exactly zero for the classical Rouse model [3]. With finite chain extensibility we get $N_2 \sim N_1/N$: the second difference is positive everywhere, although it is much smaller than N_1 .

3. Confined polymer layers: weak adsorption limit

Let us consider now a confined situation: polymer melt in a slab of thickness h between two solid surfaces, $a \ll h \ll N^{1/2}a$. Let us assume that due to favorable local interactions between polymer segments and the surfaces, the effective monomer friction constant near the surfaces, ζ_1 , is much larger than the friction constant ζ_0 in the middle part of the film: $\zeta_1 \gg \zeta_0$. We will also assume that the thickness Δ of the effective "glassy" layers near the surfaces is of order of monomer size, $\Delta \sim a$.

If the upper surface is moving with constant velocity u with respect to the bottom one, then the apparent imposed shear rate is $\dot{\gamma} = u/h$. Two basic sources of friction can be distinguished: (1) friction in the "glassy layers" $a + a$; (2) friction in the middle part of polymer layer, $h - 2a$. The friction force in a glassy layer is proportional to ζ_1 and to the surface slip velocity u_s : $\sigma_1 \sim \zeta_1 \frac{a}{v} u_s$, where $\frac{a}{v}$ is the number of monomers per unit area of "glassy layer". The velocity change in the middle part of polymer layer, $h - 2a$, is $\Delta u = u - 2u_s$, so that the effective shear rate is $\dot{\gamma}_{eff} = \frac{\Delta u}{h - 2a} \simeq \frac{u - 2u_s}{h}$. The friction force in the middle part is defined by eq. (1), where R_z^2 should be substituted by h^2 : $\sigma_2 \sim \frac{1}{v} \dot{\gamma}_{eff} \zeta_0 h^2$. Obviously σ_1 must be equal to σ_2 . However if we assume for a moment that $u_s \sim u - 2u_s \sim u$, then we get

$$\sigma_1/\sigma_2 = \frac{\zeta_1 a}{\zeta_0 h} \equiv \mu$$

The layer dynamics is thus essentially dependent on the parameter μ . The regime $\mu \ll 1$ is called here "weak adsorption" regime. Note that both inequalities $\mu \ll 1$ and $\zeta_1 \gg \zeta_0$ can be fulfilled simultaneously. Obviously in the case of weak adsorption the "bulk" friction (in the middle of the layer) is high enough in comparison with the surface friction so that the surface slip must be very strong: $u_s \simeq u/2$, the velocity gradient is concentrated in the "glassy layers", the effective shear rate is much smaller than the apparent one. The shear stress is

$$\sigma = \sigma_1 \simeq \zeta_1 \frac{a u}{v 2} \quad (9)$$

The last equation is valid as long as surface slip is strong. This ceases to be the case for very high shear velocities, $u > u^{**}$: in this regime the shear flow stretches the chains so strongly that their typical transverse size becomes much smaller than h leading to a strong reduction of the bulk friction and to elimination of the slip. In the region $u > u^{**}$ the shear stress is determined by the "bulk" equation:

$$\sigma = \eta(\dot{\gamma}) \dot{\gamma} = \frac{\tau_0}{v} \left(\frac{h}{u \tau_0} \right)^{2/3} \quad (10)$$

where $\eta(\dot{\gamma})$ is the nonlinear bulk viscosity defined in the second line of eq. (8), and $\dot{\gamma} = u/h$. A smooth crossover between equations (9) and (10) implies that

$$u^{**} \sim \frac{\tau_0^{1/2} a^{3/2}}{\tau_1^{3/2} h^{1/2}}$$

where $\tau_1 = \zeta_1 a^2$ is the typical monomer time in the glassy layers. Note that the crossover velocity between linear and non-linear regimes is decreasing as surface friction is increased; u^{**} is also decreasing as the gap h is increased.

Thus we predict the following behavior of the apparent viscosity $\eta_{app} \equiv \frac{\sigma}{\dot{\gamma}}$ in the "weak adsorption" regime:

$$\eta_{app} \sim \begin{cases} \frac{a}{v} \zeta_1 h & , u \ll u^{**} \\ \frac{\tau_0}{v} \left(\frac{h}{u\tau_0} \right)^{2/3} & , u \gg u^{**} \end{cases}$$

This prediction is in qualitative agreement with experiments and computer simulations [6-8,13].

4. Strong adsorption limit

Let us consider the case of very viscous "glassy layers", the precise condition is specified below.

Statics

It is well known that homopolymer chains obey Gaussian statistics in the melt state. In a melted layer the same is true for chain parts - blobs, g - if the blob size $ag^{1/2}$ is smaller than the layer thickness h , i.e. $g < g_0 = h^2/a^2$. A confined chain is Gaussian on scales $g < g_0$ and it is flat on larger scales, $g > g_0$.

Any monomer belonging to a thin "glassy layer" will be referred to as a contact between the chain and the corresponding surface. Gaussian statistics implies that the typical (average) number of contacts of a g_0 -blob with a surface is $n_0 \sim g_0^{1/2} = h/a$. The typical number of contacts of a smaller $g < g_0$ blob which comes close to a surface is $n(g) \sim g^{1/2}$. Number of g_0 -blobs per unit area is

$$\nu_0 = \frac{h}{v g_0} = \frac{a^2}{hv}$$

Let us distinguish between loops (chain parts between contacts with the same surface) and bridges (chain parts between contacts with different surfaces). An arbitrary conformation of a long confined chain ($N \gg g_0$) can be represented as a sequence (alternation) of bridges and attached blobs consisting of neighboring loops "grafted" to the same surface (there are of course also tail parts, but these are short). The typical number of monomers per bridge or per attached blob is g_0 .

It turns out that distribution over the sizes of attached blobs is important for dynamics. In order to find this distribution let us consider a contact (a monomer belonging to a "glassy layer"). The next surface contact might be with the same surface (with probability p') or with another surface (with probability $p = 1 - p'$). A contact with a different surface implies a bridge of $\sim g_0$ links. Thus the probability p can be estimated as the probability that an end-grafted Gaussian subchain g_0 does not contact the grafting surface any more. This probability is [14] $p \sim g_0^{-1/2}$. Therefore the probability that an attached blob consists of n loops ($n+1$ contacts) is

$$p_n = p(p')^n = p(1-p)^n \simeq p \exp(-np) \sim g_0^{-1/2} \exp(-ng_0^{-1/2}) \quad (11)$$

Taking into account that an attached g -blob typically consist of $n(g) \sim g^{1/2}$ loops we get two-dimensional concentration of attached blobs containing of order of g monomers (number of these blobs per unit area):

$$\nu(g) \sim \nu_0 n p_n \sim \frac{a g^{1/2}}{v g_0} \exp\left(-\frac{g^{1/2}}{g_0^{1/2}}\right) \quad (12)$$

Note that $\nu(g_0) \sim \nu_0$, and $\nu(1) \sim \frac{a}{v g_0}$.

Life-time of an attached blob

Let us denote $\tau(g)$ the life-time of an attached blob (the typical time during which all contacts between the blob and the surface break and the blob detaches from the surface). Obviously $\tau(1) \sim \tau_1$. In general case the detachment/attachment process of a larger blob can be considered as a diffusion along the variable $n = n(t)$, the total number of contacts. An elementary step $n \rightarrow n \pm 1$ occurs during a typical time $\Delta t \sim \tau_1/n$, since there n monomers in the surface "glassy layer" with the monomer life-time τ_1 . Eq. (11) implies that statistical weights of "states" with different n 's are nearly equal as long as $n \lesssim g_0^{1/2}$. Therefore $n(t)$ must be essentially random (rather than biased) diffusion, so that $\Delta n(t) \sim (t/\Delta t)^{1/2}$. The detachment time is given by the condition $\Delta n \sim n$:

$$\tau(g) = t \sim (\Delta t) n^2 \sim \tau_1 n \sim \tau_1 g^{1/2} \quad (13)$$

Therefore the life-time of a typical g_0 blob is

$$T_1 = \tau(g_0) \sim \tau_1 g_0^{1/2} = \tau_1 \frac{h}{a} \quad (14)$$

On the other hand relaxation (Rouse) time of a free g_0 -blob (which does not contact any surface) is

$$T_2 \sim \tau_0 g_0^2 = \tau_0 \left(\frac{h}{a}\right)^4$$

Below we assume that the surface time is much longer than the Rouse time: $T_1 \gg T_2$ ("strong adsorption limit"), i.e.

$$\frac{\tau_1}{\tau_0} \gg \left(\frac{h}{a}\right)^3 \quad (15)$$

Finally we note that T_1 is simultaneously the life-time of a typical bridge: detachment of an attached blob that typically happen during this time implies that two adjacent bridges transform to one loop.

Linear rheology

Let us again impose a motion of the upper surface with respect to the bottom one, assuming first that the velocity u is small enough. There are two main contributions to the shear stress: (1) due to elongation of bridges as the upper end of each bridge is shifting together with the upper plate it is attached to; (2) due to friction between the monomers like in the bulk. The effective maximum elongation is $\Delta x \sim u T_1$; the corresponding force per bridge is $F_b \sim \frac{\Delta x}{g_0 a^2} \sim \frac{u \tau_1}{h a}$. The bridge contribution to the stress is proportional to F_b and the concentration of bridges: $\sigma_1 \simeq \nu_0 F_b \sim \frac{a}{v} \frac{u \tau_1}{h^2}$. The bulk contribution due to friction between loops and bridges can be estimated using eq. (1) with h instead of R_z , and $\dot{\gamma} = u/h$:

$$\sigma_2 \sim \dot{\gamma} \eta^* \sim \frac{u}{h} \frac{\zeta_0}{v} h^2 \quad (16)$$

Note that $\sigma_2/\sigma_1 \sim \frac{\tau_0}{\tau_1} \left(\frac{h}{a}\right)^3$, i.e. $\sigma_2/\sigma_1 \ll 1$: the bulk contribution to the *linear* friction is negligible in the "strong adsorption regime" (see ineq. (15)). Thus the shear stress is dominated by the elasticity of the bridges:

$$\sigma \simeq \sigma_1 \sim \frac{a u \tau_1}{v h^2} \quad (17)$$

Eq. (17) is valid if the typical bridge elongation during the life-time, Δx , is smaller than the bridge contour length $\sim g_0 a$, $\Delta x \ll g_0 a$, i.e. $u \ll u_1 \sim h/\tau_1$.

Non-linear rheology

In the regime of higher velocities, $u \gg u_1$, the bridges completely elongate during the time $t^* = \frac{g_0 a}{u}$ which is much shorter than the equilibrium bridge life-time T_1 . The average force during the elongation process is $F_b \sim \frac{\Delta x}{g_0 a^2} \sim \frac{g_0 a}{g_0 a^2} = \frac{1}{a}$. This force can not induce any noticeable "creep" of the attached blobs (at the ends of the bridge): in fact even if we assume that the whole F_b is applied to the very end monomer of the bridge situated in the "glassy layer" near one of surfaces, the corresponding slip velocity of the monomer would be $v_s = \frac{F_b}{\zeta_1} \sim \frac{1}{a \zeta_1} \ll u_1 = \frac{h}{\zeta_1 a^2}$. Therefore both attached blobs at the bridge ends are essentially "grafted" to the surfaces during the elongation process. However as soon as the complete elongation of a bridge is achieved, both blobs must start to move with respect to the surfaces with the velocities $u/2$, hence the elongation force must sharply increase, and at least one of the attached blobs rapidly detach from the corresponding surface.

The typical life-time of an attached blob is thus t^* (or smaller) in the non-linear regime $u \gg u_1$. Therefore a large attached blob of size, say, g_0 , could not possibly appear in this case: the attachment time of a g_0 -blob is $T_1 \gg t^*$, so that the blob just do not have enough time to be attached: it will be pulled from the surface by the bridge elongation force much earlier. Only blobs which are small enough could possibly attach to a surface. Obviously the typical (terminal) size, g^* , of an attached blob is determined by the condition $\tau(g^*) \sim t^*$, that is $\tau_1 (g^*)^{1/2} \sim t^*$, or

$$g^* \sim \left(\frac{h^2}{u a \tau_1} \right)^2$$

Using eq. (12) we find that the bridge concentration, ν_b (which is equal to concentration of attached blobs) is decreasing with u :

$$\nu_b \sim \nu(g^*) \sim \nu_0 \left(\frac{g^*}{g_0} \right)^{1/2} \sim \frac{a^2}{v \tau_1} \frac{1}{u}$$

The shear stress contribution due to bridges is

$$\sigma_1 = \nu_b F_b \sim \frac{1}{v} \frac{a}{\tau_1 u} \quad (18)$$

The total stress is the sum of two contributions σ_1 and σ_2 , given by eqs. (16), (18):

$$\sigma = \sigma_1 + \sigma_2 = \frac{1}{v} \left(\frac{a}{u \tau_1} + \frac{h u \tau_0}{a^2} \right)$$

Note that the stress decreases with u in the region $u_1 < u < u_{\min}$, and attains a local minimum at

$$u = u_{\min} \sim \frac{a^{3/2}}{h^{1/2} (\tau_0 \tau_1)^{1/2}}$$

In the region $u > u_{\min}$ the stress contribution due to friction between loops (σ_2) dominates the bridge contribution (σ_1) which is small since most of the bridges are effectively destroyed by the flow in this regime.

At even higher velocities, $u > u_2$, the flow strongly elongates the loops along the stream, and simultaneously compress them in the transverse (z) direction. The crossover velocity u_2 is determined by condition $R_z\left(\frac{u}{h}\right) = h$, where $\frac{u}{h} = \dot{\gamma}$ is the shear rate, and $R_z(\dot{\gamma})$ is defined by eq. (6). Thus we get

$$u_2 \sim \frac{a}{\tau_0} \frac{a^2}{h^2}$$

The shear stress in the non-linear regime, $u > u_2$, is defined by the "bulk" equation (7) with $\dot{\gamma} = u/h$:

$$\sigma \sim \frac{1}{v} \left(\frac{u\tau_0}{h} \right)^{1/3}$$

Thus we predict the following dependence of the shear stress on shear velocity in the "strong adsorption" regime:

$$\sigma \sim \begin{cases} \frac{a}{v} \frac{u\tau_1}{h^2} & , u < u_1 \\ \frac{1}{v} \left(\frac{a}{u\tau_1} \right) & , u_1 < u < u_{\min} \\ \frac{1}{v} \frac{h\tau_0 u}{a^2} & , u_{\min} < u < u_2 \\ \frac{1}{v} \left(\frac{u\tau_0}{h} \right)^{1/3} & , u > u_2 \end{cases} \quad (19)$$

The shear stress is increasing from $\sigma = 0$ to $\sigma = \sigma_{\max} \sim \frac{1}{v} \frac{a}{h}$ as the velocity in creased from 0 to u_1 , then in the region $u_1 < u < u_{\min}$ the stress is *decreasing* from σ_{\max} to $\sigma_{\min} \sim \frac{1}{v} \left(\frac{h\tau_0}{a\tau_1} \right)^{1/2}$, then the stress is increasing again nearly linearly with u back to σ_{\max} at $u \sim u_2$; finally the stress follows $u^{1/3}$ law for $u > u_2$. Note that σ_{\max} is much larger than σ_{\min} : $\sigma_{\max}/\sigma_{\min} \sim \left(\frac{\tau_1 a^3}{\tau_0 h^3} \right)^{1/2} \gg 1$, see ineq. (15). Note also that $\sigma_{\max}/\sigma_{\min} \sim u_{\min}/u_1 \sim u_2/u_{\min}$.

Both decrease and increase of shear stress vs. shear rate was observed while shearing thin polymer films [15], however the reported experimental data are not extensive enough to allow a systematic comparison.

Let us consider the situation under stress-control conditions: a constant shear stress is applied to the film. As the stress is increased from zero to σ_{\max} the shear velocity must continuously (and linear) increase from 0 to u_1 . However the only stationary velocity corresponding to a larger stress $\sigma > \sigma_{\max}$ is $u > u_2$. Therefore the velocity jumps from u_1 to u_2 at $\sigma = \sigma_{\max}$. In the region $\sigma > \sigma_{\max}$ the velocity is rapidly increasing as σ^3 . Thus σ_{\max} can be considered as a sort of "yield stress" for the layer: in the regime $\sigma < \sigma_{\max}$ the behavior is more "solid-like" (elongation of bridges + slow creep), whereas for $\sigma > \sigma_{\max}$ the system suddenly becomes much less viscous because here nearly all bridges must be broken by the flow ("fluid-like" behavior). Note that the "yield stress" is inverse proportional to the layer thickness h , and thus is tending to 0 in the bulk limit.

5. Stick-slip motion

It is well-known [16] that a stationary sliding motion might become unstable in the regime when the friction force is decreasing with the imposed velocity. Below

we show that this is indeed the case for shearing dynamics of polymer layers in the "strong adsorption" limit. Normally a sliding velocity $u_0(t)$ is applied to the system via a mechanical coupling – an effective elastic spring κ . The stress implied by the spring deformation $x_0(t) - x(t)$ is $\sigma = \kappa(x_0(t) - x(t))$, where $x_0(t) = u_0 t$ is the imposed shear displacement, and $x(t)$ is the actual displacement of one layer surface with respect to another, so that $u = \frac{dx(t)}{dt}$ is the actual shear velocity.

Let us assume that the imposed velocity corresponds to the regime where the stationary stress is decreasing with u : $u_1 \ll u_0 \ll u_{min}$, and that the initial stress is small, $\sigma \ll \sigma_{max}$. Then as long as the stress σ is smaller than σ_{max} , the actual velocity u is smaller than u_1 . Therefore here $\frac{d\sigma}{dt} = \kappa \left(\frac{dx_0}{dt} - \frac{dx}{dt} \right) = \kappa(u_0 - u) \simeq \kappa u_0$, so that the stress is nearly linearly increasing with time: $\sigma \simeq \sigma(0) + \kappa u_0 t$. The stress grows up to σ_{max} during the time $t_1 \simeq \frac{\sigma_{max}}{\kappa u_0}$. As soon as the stress exceeds σ_{max} , the actual velocity jumps to a much higher value $u_2 \gg u_1$; simultaneously nearly all bridges break. Therefore the stress starts to rapidly decrease for $t > t_1$, since $\frac{d\sigma}{dt} = \kappa(u_0 - u) \simeq -\kappa u$ in this regime. The actual velocity follows the same branch, $u_{min} < u < u_2$, it switched to at $t = t_1$ until the stress falls down to $\sigma = \sigma_{min}$. At this moment ($t = t_2$) the actual velocity switches back to the low-velocity branch ($u < u_1$); the velocity at $t = t_2$ can be found using eq. (19): $u \sim \frac{h^{2.5} \tau_1^{0.5}}{a^{1.5} \tau_1^{1.5}} \ll u_1$. At this point the bridges start to restore, and the whole cycle repeats again.

The type of motion described above is called a stick-slip motion [17,18]: The stress is periodically changes with time, each period consisting of two stages: (1) stick, linear increase of the stress due to deformation of an elastic coupling (spring), $0 < t < t_1$; (2) slip, a rapid decrease of the stress down to σ_{min} , $t_1 < t < t_2$. As the second stage is much faster than the first one, the total period T_{ss} of the stick-slip motion is close to t_1 :

$$T_{ss} \simeq t_1 = \frac{\sigma_{max}}{\kappa u_0} \sim \frac{1}{v} \frac{a}{h} \frac{1}{\kappa u_0} \quad (20)$$

Note that the period is inverse proportional to the imposed velocity.

The dynamical picture described above is valid if the bridges have enough time to restore during the first stage t_1 , i.e. if t_1 is much larger than the bridge (attached blob) relaxation time T_1 . The last condition ($t_1 \gg T_1$) can be rewritten using eqs. (14), (20) as $u_0 < u^*$, where

$$u^* = \frac{1}{v} \frac{1}{\tau_1} \left(\frac{a}{h} \right)^2 \frac{1}{\kappa}$$

Two conditions mentioned above, $u_0 > u_1$ and $u_0 < u^*$ are compatible only if $u^* > u_1$, i.e. if

$$\kappa < \kappa^* \sim \frac{a^2}{v h^3} \quad (21)$$

Thus a stick-slip motion is predicted in a limited range of imposed velocities if the elastic coupling constant is not too large ($\kappa < \kappa^*$) in qualitative agreement with experimental observations [4,19–21]. Note that the last condition is not too strong if the layer thickness h is small enough.

6. Conclusions

(1) A simple scaling behavior of the non-linear viscosity, $\eta \propto \dot{\gamma}^{-2/3}$ if $\dot{\gamma} > \dot{\gamma}^*$, is predicted in a melt of Rouse polymer chains with finite contour length; the critical shear rate $\dot{\gamma}^*$ is proportional to $N^{-3/2}$.

(2) The same scaling behavior is also predicted for thin polymer layers if the surface friction is moderate ("weak adsorption" regime); in this case the critical shear rate is inverse proportional to the surface friction constant in the power 1.5.

(3) A non-monotonous stress vs. shear velocity behavior is predicted for the case of high surface friction; in this case the layer rheology is characterized by an effective "yield stress" which is inverse proportional to the layer thickness.

(4) A stick-slip periodical motion under a constant imposed velocity is predicted for the case of low enough elastic coupling constant κ ; the process can be considered as an alternation of bridge formation and bridge breakage stages.

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